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(54) **Process for making ethylene oxide-capped polyols from double metal cyanide-catalyzed polyols**

Verfahren zur Herstellung von Ethylenoxid verkappten Polyolen aus Doppelmetallcyanid katalysierten Polyolen

Procédé pour la préparation de polyols ayant des groupes terminaux à partir d'oxyde d'éthylène et préparés à partir de polyols catalysés avec des catalyseurs de métal double

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Description

FIELD OF THE INVENTION

[0001] The invention relates to a process for making polyether polyols that have a high content of primary hydroxyl groups. In particular, the invention is a process for making ethylene oxide-capped polyols from polyols prepared by double metal cyanide catalysis.

BACKGROUND OF THE INVENTION

[0002] Ethylene oxide-capped polyols have long been valuable in the polyurethane industry because of the favorable reactivity of their primary hydroxyl groups with polyisocyanates. EO-capped polyols are normally made in two steps. First, propylene oxide (or a mixture of propylene oxide and ethylene oxide) is polymerized in the presence of a basic catalyst (usually potassium hydroxide) to produce a polyol that contains mostly or exclusively secondary hydroxyl groups. Second, ethylene oxide is added to the catalyst-containing mixture to convert some or most of the secondary hydroxyl groups to primary hydroxyl groups. The process conveniently uses the same catalyst (usually KOH) for both the propoxylation and ethoxylation steps.

[0003] Double metal cyanide (DMC) catalysts such as zinc hexacyanocobaltate offer many advantages for making polyether polyols. Polyols with exceptionally low unsaturation levels compared with KOH polyols can be made. The advantages of low-unsaturation polyols for making polyurethanes with improved properties are well documented. DMC catalysts also have exceptional activity, so polyol production is efficient. The best DMC catalysts now known are active enough to be used at such low concentrations that back-end purification of the polyols is often unnecessary.

[0004] In spite of the many advantages of DMC catalysts for making polyether polyols, an important drawback remains: ethylene oxide-capped polyols cannot be made directly using a DMC catalyst. In other words, one cannot prepare an oxypropylene polyol by DMC catalysis, and then simply add EO to cap the polyol (as is done with KOH). When EO is added to an polyoxypropylene polyol made with a DMC catalyst, the resulting product is a heterogeneous mixture of: (1) mostly unreacted polyoxypropylene polyol; and (2) a minor proportion of highly ethoxylated polyoxypropylene polyol and/or polyethylene oxide.

[0005] The usual way to make an EO-capped polyol from a DMC-catalyzed polyol involves recatalysis. See, for example, U.S. Pat. Nos. 4,355,188 and 4,721,818. First, an oxypropylene polyol (or random EO-PO copolymer) is made by DMC catalysis. Second, a basic catalyst such as an alkali metal, alkali metal hydride, alkali metal alkoxide, alkali metal hydroxide, or the like, is added. The basic catalyst deactivates the DMC catalyst. Typically, the polyol must then be stripped to remove wa-

ter or alcohol introduced (even in trace amounts) with the basic catalyst. Finally, ethylene oxide is added to cap the polyol with oxyethylene units.

[0006] The recatalysis approach has some important disadvantages. First, many basic catalysts (particularly the alkali metals and alkali metal hydrides) are highly reactive, moisture-sensitive, and difficult to handle safely. Second, a dedicated reactor is needed for base-catalyzed EO capping because DMC catalysts are poisoned by even trace amounts of residual base. Thus, a reactor used for base-catalyzed EO capping must be cleaned scrupulously before another DMC-catalyzed reaction can be performed in the same reactor. On a large scale, this is impractical, so a dedicated reactor just for EO-capping is needed. Third, stripping polyols to remove water or alcohol is time consuming, energy intensive, and often gives sporadic results. Incomplete stripping gives hazy polyols that contain polyethylene oxide (reaction product of traces of water or alcohol with ethylene oxide), and hazy polyols are commercially undesirable.

[0007] An improved process for making EO-capped polyols from DMC-catalyzed polyols is needed. Preferably, the process would overcome the need for recatalysis. It would avoid highly reactive, moisture-sensitive ethoxylation catalysts, and would eliminate the need to strip water or alcohols from the polyol intermediate prior to addition of ethylene oxide. A preferred process would not require a dedicated reactor just for EO-capping. Ideally, the process would be easy to practice, and would provide a way to make low unsaturation polyols with high primary hydroxyl group contents.

SUMMARY OF THE INVENTION

[0008] This invention provides a process for making an ethylene oxide-capped polyol, said process comprising:

- a) blending a first polyol that is made by double metal cyanide (DMC) catalysis and contains active DMC catalyst with a second polyol that is made by basic catalysis and contains the basic catalyst used to make the second polyol in an amount from 0.05 to 2 wt. % of the polyol blend; and
- b) reacting the resultant polyol blend, without prior stripping of water or alcohols from the blend, with ethylene oxide to produce the ethylene oxide-capped polyol, optionally after first reacting said resultant polyol blend with another alkylene oxide. This invention further provides use of a second polyol that is made by basic catalysis and contains the basic catalyst used to make the second polyol in an amount from 0.05 to 2 wt. % of the polyol blend to prepare an ethylene oxide-capped polyol by blending it with a first polyol that is made by double metal cyanide (DMC) catalysis and contains active DMC catalyst; and reacting the resulting polyol

blend, without prior stripping of water or alcohols from the blend, with ethylene oxide to produce the ethylene oxide-capped polyol, optionally after first reacting said resulting polyol blend with another alkylene oxide.

[0009] In accordance with the present invention, it has surprisingly been found that DMC-catalyzed polyols, which cannot be directly ethoxylated, are capped successfully by first blending them with base-containing polyols, and then adding ethylene oxide to the polyol blends. The process of the invention overcomes some of the key drawbacks of the recatalysis approach to EO-capping DMC polyols. First, the invention overcomes any need to use reactive metals or metal hydrides; the basic catalyst (usually potassium hydroxide) used to make the second polyol catalyzes the ethoxylation. Second, because the reactor used for ethoxylating the polyol blends can also be used to make the base-catalyzed polyol component of the blend, a dedicated reactor is not needed just for EO-capping. Third, and most important, the process of the invention eliminates the need to strip water or alcohols from polyol intermediates prior to ethoxylation.

[0010] The invention provides a simple, effective way to make polyols that have reduced unsaturation levels (as a result of their preparation in part by DMC catalysis), and high primary hydroxyl group contents.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The invention is a process for making an ethylene oxide-capped polyol by ethoxylating a blend of polyols. The polyol blend comprises a first polyol that contains an active double metal cyanide catalyst, and a second polyol that contains a basic catalyst. The polyol blend is reacted with ethylene oxide to produce an ethylene oxide-capped polyol.

[0012] The first polyol is made using a double metal cyanide (DMC) catalyst. Generally, any known DMC catalyst can be used. Suitable DMC catalysts are well known in the art. Catalysts and methods for preparing them are described fully in U.S. Pat. Nos. 3,427,256, 3,427,335, 3,829,505, 4,477,589, and 5,158,922. Zinc hexacyanocobaltate catalysts are preferred. Recently, highly active DMC catalysts have been developed, as described, for example, in copending EP-A-0654302, and these catalysts are advantageously used to make the first polyol.

[0013] The first polyol is prepared by methods commonly known in the art. A heterocyclic monomer (usually an epoxide) reacts with an active hydrogen-containing initiator (typically a low molecular weight polyol) in the presence of a DMC catalyst to produce the first polyol. Suitable heterocyclic monomers, active hydrogen-containing initiators, and methods for making polyether polyols using DMC catalysts appear in U.S. Pat. Nos. 3,829,505, 3,941,849, 4,355,188, and 4,472,560.

[0014] The first polyol is any polyether polyol that can be made by DMC catalysis. Preferred first polyols are polyoxypropylene polyols and random copolymers of propylene oxide and ethylene oxide. The first polyol preferably has a nominal functionality from 2 to 8, more preferably from 2 to 3. The first polyol generally has a hydroxyl number within the range of 5 to 500 mg KOH/g, more preferably from 10 to 100 mg KOH/g. The first polyol generally has a number average molecular weight within the range of 200 to 25,000, more preferably from 500 to 10,000. The first polyol generally has a low level of unsaturation, typically less than about 0.04 meq/g, preferably less than about 0.02 meq/g, and more preferably less than about 0.01 meq/g.

[0015] The first polyol is blended with a second polyol. The second polyol is prepared using a basic catalyst by methods well known to those skilled in the art of making conventional polyether polyols. A heterocyclic monomer (usually an epoxide) reacts with an active hydrogen-containing initiator (typically a low molecular weight polyol) in the presence of a basic catalyst to produce the second polyol. Suitable heterocyclic monomers, active hydrogen-containing initiators, basic catalysts, and methods for making polyethers using basic catalysts appear in U.S. Pat. Nos. 4,495,081, 4,687,851, 3,317,508, and 3,445,525. Preferably, the second polyether is prepared using an alkali metal hydroxide (such as potassium hydroxide) as the basic catalyst.

[0016] The second polyol is any polyether polyol that can be made by basic catalysis. Preferred second polyols are polyoxypropylene polyols, random copolymers of propylene oxide and ethylene oxide, and EO-capped polyols. The second polyol preferably has a nominal functionality from 2 to 8, more preferably from 2 to 3. The second polyol generally has a hydroxyl number within the range of 20 to 1800 mg KOH/g, more preferably from 30 to 500 mg KOH/g. The second polyol generally has a number average molecular weight within the range of 76 to 8000, more preferably from 500 to 6000.

[0017] The first and second polyols are blended together by any suitable means. Preferably, the polyols are miscible. Generally, the polyols need not have the same or similar functionalities, hydroxyl numbers, or molecular weights. For some applications, it may be advantageous to use a first and second polyol that have very different characteristics. On the other hand, it is often convenient to blend polyols having about the same hydroxyl number to simplify the process of formulating polyurethanes.

[0018] The relative amounts of first and second polyols in the blend can vary within wide limits. Generally, it is preferred to use from 10 to 90 wt.% of the first polyol and from 10 to 90 wt.% of the second polyol in the blend. More preferably, the blend contains from 30 to 70 wt.% of the first polyol and from 30 to 70 wt.% of the second polyol.

[0019] When the polyols are blended together, some of the basic catalyst in the second polyol deactivates the

DMC catalyst in the first polyol. The rest of the basic catalyst is available for catalyzing ethoxylation of the polyol blend. The basic catalyst, typically KOH, is present in the polyol blend in an amount within the range of 0.05 to 2 wt.%, which is sufficient for the ethylene oxide capping step. A more preferred range is from 0.1 to 1.0 wt.%.

[0020] In the second step of the process of the invention, the polyol blend reacts with ethylene oxide to produce an ethylene oxide-capped polyol. The amount of ethylene oxide (EO) used to cap the polyol depends on many factors, including the desired oxyethylene content of the polyether, the desired primary hydroxyl group content, the polyol molecular weights and functionalities, and other factors. Generally, the amount of EO used will be within the range of 5 to 30 wt.% based on the amount of ethylene oxide-capped polyol.

[0021] The process of the invention is used to make polyether polyols having a high content of primary hydroxyl groups. The proportion of primary hydroxyl groups needed for a particular use varies. Typically, products having at least 50%, such as from 50% to 95%, primary hydroxyl groups are needed, preferably having at least 70%, such as from 70% to 90%. These products can be made with the process of the invention.

[0022] The ethoxylation step is generally performed by heating the blend of first and second polyols to the desired reaction temperature, and adding ethylene oxide incrementally to the mixture. The technique is essentially the same as is now practiced for capping polyols with ethylene oxide using a basic catalyst. A suitable method is described, for example, in U.S. Pat. No. 4,355,188. The reaction temperature is typically within the range of 50°C to 220°C. After EO addition is complete, the reaction is generally held at the same or a higher temperature to complete the polymerization.

[0023] Following ethoxylation, the EO-capped product is typically purified to remove catalyst residues. Any suitable means of purifying the polyol can be used, including treatment with an ion-exchange resin, water washing, or treatment with an adsorbent such as magnesium silicate. Suitable methods for purifying the EO-capped polyols are described, for example, in U.S. Pat. Nos. 3,715,402, 3,823,145, 4,721,818, and 4,355,188.

[0024] The polyether polyols made by the process of the invention have a high content of primary hydroxyl groups. This feature makes them valuable for polyurethane applications that require a "reactive" polyol. At the same time, the polyols have significantly lower unsaturation levels than polyols made using only a basic catalyst. When very low unsaturations are required, the relative proportion of DMC-catalyzed polyol in the blend is simply increased. Low unsaturation polyols such as the ones made by the process of the invention offer many well-recognized advantages for polyurethanes, including improved tensile properties and lower compression sets.

[0025] High-primary, low-unsaturation polyols were

available previously, but only by a recatalysis procedure that requires careful stripping prior to ethoxylation. Even with good stripping, the recatalysis approach often gives hazy polyols. The process of the invention surprisingly gives polyols with high primary hydroxyl group content and low unsaturation. In addition, the process of the invention gives haze-free products without requiring a stripping step.

[0026] The polyols made by the process of the invention are particularly useful for making polyurethane foams, elastomers, sealants, coatings, and adhesives. The polyols are especially valuable for making molded polyurethane foams, which are made at relatively cool temperatures and require a high content of primary hydroxyl groups for adequate reactivity.

[0027] The following example illustrates the invention.

EXAMPLE 1

[0028] A one-liter Parr reactor is charged with a polyoxypropylene triol (247 g) having a hydroxyl number of 41.5 mg KOH/g and an unsaturation of 0.008 meq/g, and which contains 25 ppm of active zinc hexacyanocobaltate catalyst. The reactor is also charged with a crude glycerin-started polyoxypropylene triol (134 g) that is made by KOH catalysis, and has a hydroxyl number of 41.5 mg KOH/g, an unsaturation of 0.046 meq/g, and a KOH content of 0.71 wt.%.

[0029] The polyol mixture is heated to 117°C, and propylene oxide (20 g) is added. After 45 min., the temperature is increased to 125°C, and the mixture is kept at 125°C for 90 min. Nitrogen is bled into the reactor until the pressure in the reactor is about 1480 kPa (20 psig). Ethylene oxide (100 g) is added to the reactor at a rate of 1 g/min, and the mixture is kept at 125°C for an additional hour following the EO addition. The product (491 g) is refined by passing it through an activated styrene/divinylbenzene cation-exchange resin.

[0030] The refined polyol has a hydroxyl number of 33 mg KOH/g, an unsaturation of 0.017 meq/g, an oxyethylene content of 20.5 wt.%, and a primary hydroxyl group content of 80%. The product is free of haze, and remains clear for months.

Claims

1. A process for making an ethylene oxide-capped polyol, said process comprising:

- a) blending a first polyol that is made by double metal cyanide (DMC) catalysis and contains active DMC catalyst with a second polyol that is made by basic catalysis and contains the basic catalyst used to make the second polyol in an amount from 0.05 to 2 wt. % of the polyol blend; and
- b) reacting the resultant polyol blend, without

prior stripping of water or alcohols from the blend, with ethylene oxide to produce the ethylene oxide-capped polyol, optionally after first reacting said resultant polyol blend with another alkylene oxide.

2. A process as claimed in claim 1 characterised in that the first polyol is selected from polyoxypropylene polyols and random copolymers of propylene oxide and ethylene oxide. 5
3. A process as claimed in claim 1 or claim 2 characterised in that the first polyol contains a zinc hexacyanocobaltate catalyst. 10
4. A process as claimed in any one of the preceding claims characterised in that the second polyol contains an alkali metal hydroxide catalyst. 15
5. A process as claimed in any one of the preceding claims characterised in that the polyol blend contains from 10 to 90 wt. % of the first polyol and from 10 to 90 wt. % of the second polyol. 20
6. A process as claimed in claim 5 characterised in that the polyol blend contains from 30 to 70 wt. % of the first polyol and from 30 to 70 wt. % of the second polyol. 25
7. A process as claimed in any one of the preceding claims characterised in that the amount of ethylene oxide used in step (b) is within the range of 5 to 30 wt. % based on the amount of ethylene oxide-capped polyol. 30
8. A process as claimed in any one of the preceding claims characterised in that the ethylene oxide-capped polyol has at least 50% primary hydroxyl end groups. 35
9. A process as claimed in claim 8 characterised in that the ethylene oxide-capped polyol has at least 70% primary hydroxyl end groups. 40
10. Use of a second polyol that is made by basic catalysis and contains the basic catalyst used to make the second polyol in an amount from 0.05 to 2 wt. % of the polyol blend to prepare an ethylene oxide-capped polyol by blending it with a first polyol that is made by double metal cyanide (DMC) catalysis and contains active DMC catalyst; and reacting the resulting polyol blend, without prior stripping of water or alcohols from the blend, with ethylene oxide to produce the ethylene oxide-capped polyol, optionally after first reacting said resulting polyol blend with another alkylene oxide. 45
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Patentansprüche

1. Verfahren zur Herstellung eines Ethylenoxid-verkappten Polyols, umfassend:
 - a) das Vermischen eines ersten Polyols, das durch Doppelmetallcyanid-(DMC)-Katalyse hergestellt wird und aktiven DMC-Katalysator enthält, mit einem zweiten Polyol, das durch basische Katalyse hergestellt wird und den basischen Katalysator, der zur Herstellung des zweiten Polyols verwendet wird, in einer Menge von 0,05 bis 2 Gew.-% der Polyol-Mischung enthält; und
 - b) das Umsetzen der sich ergebenden Polyol-Mischung, ohne dass vorher Wasser oder Alkohole von der Mischung mit Ethylenoxid abgestrippt werden, um das Ethylenoxid-verkappte Polyol herzustellen, gegebenenfalls nachdem zuerst die sich ergebende Polyol-Mischung mit einem anderen Alkylenoxid umgesetzt wurde.
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass das erste Polyol aus Polyoxypropylenpolyolen und statistischen Copolymeren von Propylenoxid und Ethylenoxid ausgewählt ist.
3. Verfahren gemäß Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, dass das erste Polyol einen Zinkhexacyanocobaltat-Katalysator enthält.
4. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass das zweite Polyol einen Alkalimetallhydroxid-Katalysator enthält.
5. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die Polyol-Mischung 10 bis 90 Gew.-% des ersten Polyols und 10 bis 90 Gew.-% des zweiten Polyols enthält.
6. Verfahren gemäß Anspruch 5, dadurch gekennzeichnet, dass die Polyol-Mischung 30 bis 70 Gew.-% des ersten Polyols und 30 bis 70 Gew.-% des zweiten Polyols enthält.
7. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass die Menge des in der Stufe (b) verwendeten Ethylenoxids im Bereich von 5 bis 30 Gew.-%, bezogen auf die Menge des Ethylenoxid-verkappten Polyols, liegt.
8. Verfahren gemäß irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, dass das Ethylenoxid-verkappte Polyol wenigstens 50 % pri-

märe Hydroxylendgruppen aufweist.

9. Verfahren gemäß Anspruch 8, dadurch gekennzeichnet, dass das Ethylenoxid-verkappte Polyol wenigstens 70 % primäre Hydroxylendgruppen aufweist.

10. Verwendung eines zweiten Polyols, das durch basische Katalyse hergestellt wird und den zur Herstellung des sekundären Polyols verwendeten basischen Katalysator in einer Menge von 0,05 bis 2 Gew.-% der Polyol-Mischung enthält, um ein Ethylenoxid-verkapptes Polyol herzustellen, indem man das zweite Polyol mit einem ersten Polyol vermischt, das durch die Doppelmetallcyanid(DMC)-Katalyse hergestellt wird und aktiven DMC-Katalysator enthält, und die sich ergebende Polyol-Mischung ohne dass vorher Wasser und Alkohole aus der Mischung mit Ethylenoxid abgestrippt wurden - mit Ethylenoxid umgesetzt, um das Ethylenoxid-verkappte Polyol herzustellen, gegebenenfalls nachdem zuerst die sich ergebende Polyol-Mischung mit einem anderen Alkylenoxid umgesetzt wurde.

Revendications

1. Procédé pour la fabrication d'un polyol à terminaison oxyde d'éthylène, ledit procédé comprenant :

- a) le mélange d'un premier polyol qui est fabriqué par un catalyseur de cyanure de métal double (DMC) et qui contient un catalyseur DMC actif avec un second polyol qui est fabriqué par catalyse basique et qui contient le catalyseur basique utilisé pour fabriquer le second polyol dans une quantité de 0,05 à 2% en poids du mélange de polyols; et
b) la réaction du mélange de polyols résultant sans purifier préalablement le mélange de l'eau ou des alcools avec de l'oxyde d'éthylène pour produire le polyol à terminaison oxyde d'éthylène, facultativement après une première réaction dudit mélange résultant de polyols avec un autre oxyde d'alkylène.

2. Procédé selon la revendication 1, caractérisé en ce que le premier polyol est choisi parmi des polyoxypropylènepolyols et des copolymères statistiques d'oxyde de propylène et d'oxyde d'éthylène.

3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que le premier polyol contient un catalyseur d'hexacyanocobaltate de zinc.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le second poly-

ol contient un catalyseur d'hydroxyde de métal alcalin.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le mélange de polyols contient de 10 à 90% en poids du premier polyol et de 10 à 90% en poids du second polyol.

6. Procédé selon la revendication 5, caractérisé en ce que le mélange de polyols contient de 30 à 70% en poids du premier polyol et de 30 à 70% en poids du second polyol.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité d'oxyde d'éthylène utilisé dans l'étape (b) se trouve dans l'intervalle de 5 à 30% en poids rapportés à la quantité de polyol à terminaison oxyde d'éthylène.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le polyol à terminaison oxyde d'éthylène présente au moins 50% de groupes terminaux hydroxyle primaire.

9. Procédé selon la revendication 8, caractérisé en ce que le polyol à terminaison oxyde d'éthylène présente au moins 70% de groupes terminaux hydroxyle primaire.

10. Utilisation d'un second polyol qui est fabriqué par une catalyse basique et qui contient le catalyseur basique utilisé pour fabriquer le second polyol dans une quantité de 0,05 à 2% en poids du mélange de polyols pour préparer un polyol à terminaison oxyde d'éthylène en le mélangeant avec un premier polyol qui est fabriqué par une catalyse au cyanure de métal double (DMC) et qui contient un catalyseur DMC actif; et la réaction du mélange résultant de polyols sans purifier préalablement le mélange de l'eau et des alcools avec de l'oxyde d'éthylène pour produire le polyol à terminaison oxyde d'éthylène, facultativement après une première réaction dudit mélange résultant de polyols avec un autre oxyde d'alkylène.